

Supporting Information

Efficient Synthesis of (*R*)-Harmonine – the toxic principle of the multicolored Asian lady beetle (*Harmonia axyridis*)

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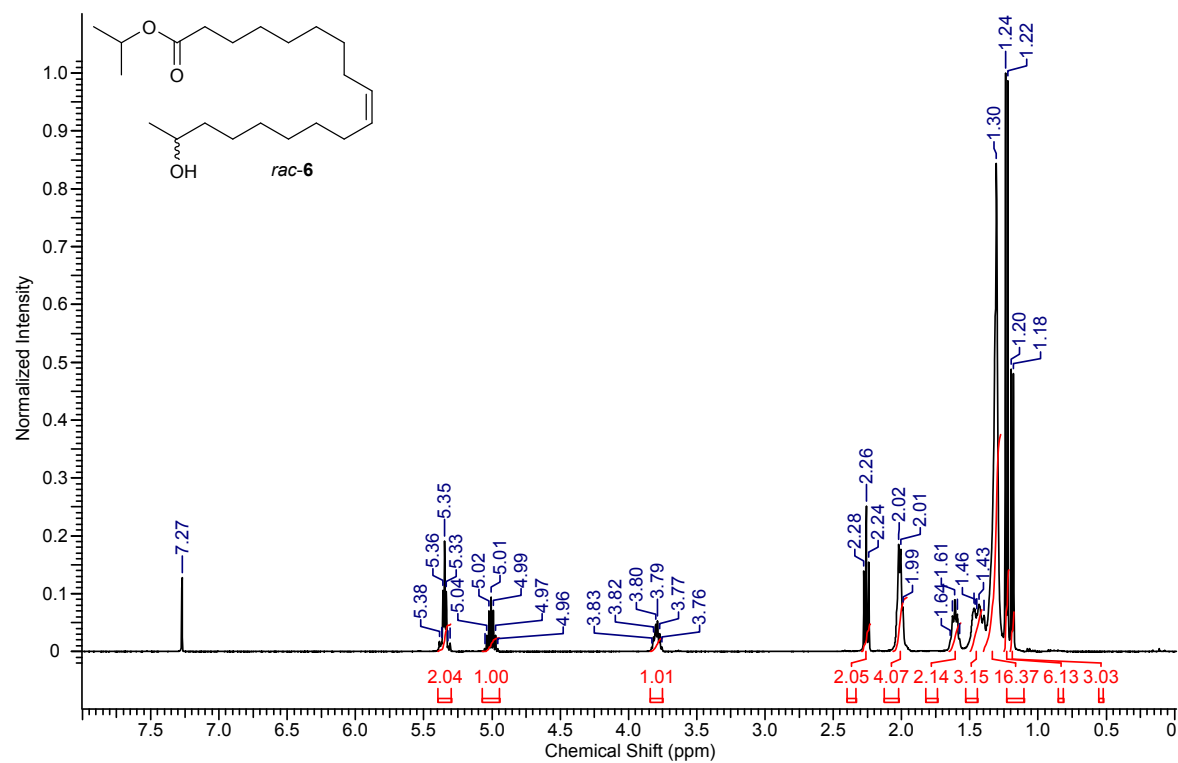
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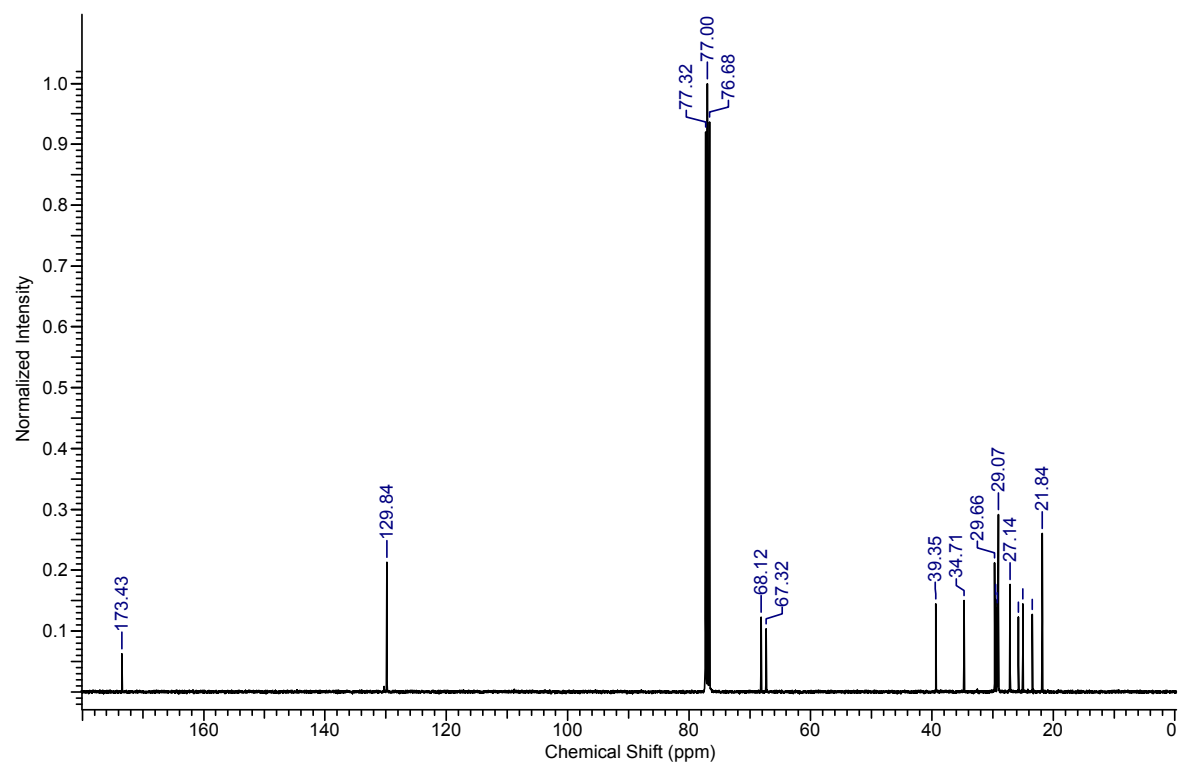
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MS data	S12
Determination of the ee of (<i>R</i>)- 9	S13
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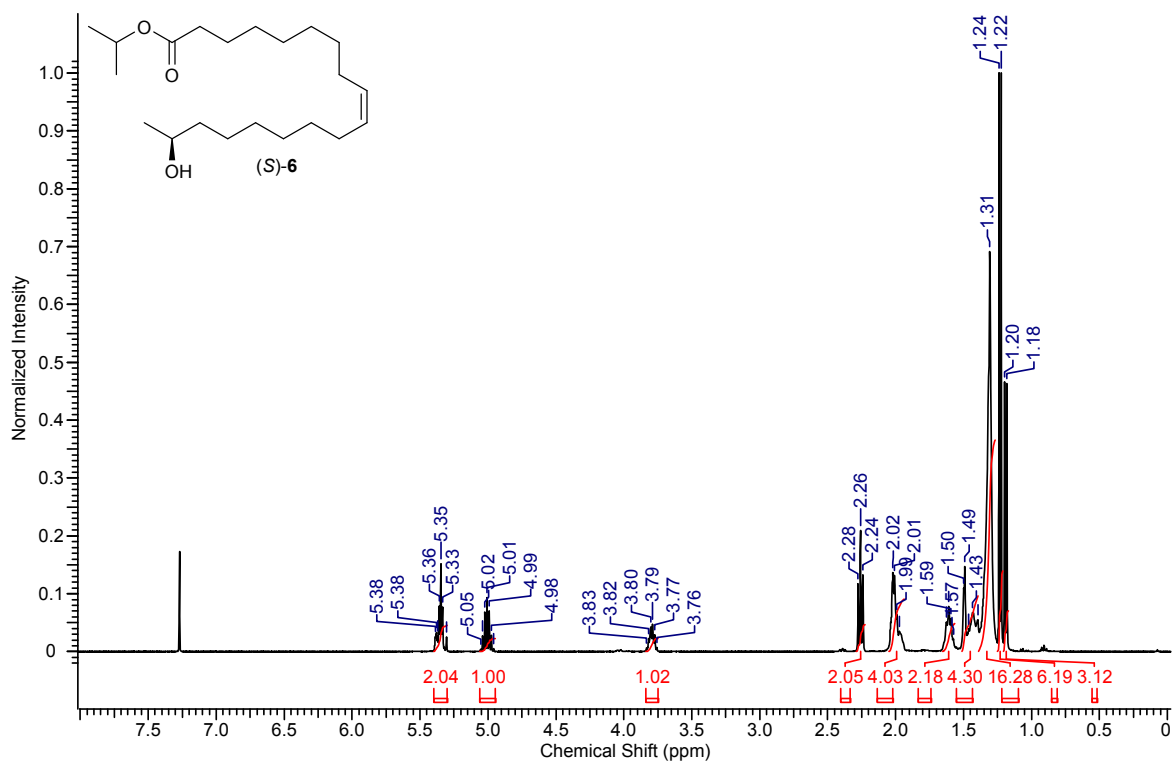
^1H NMR spectrum of compound *rac-6* in CDCl_3 (400 MHz)



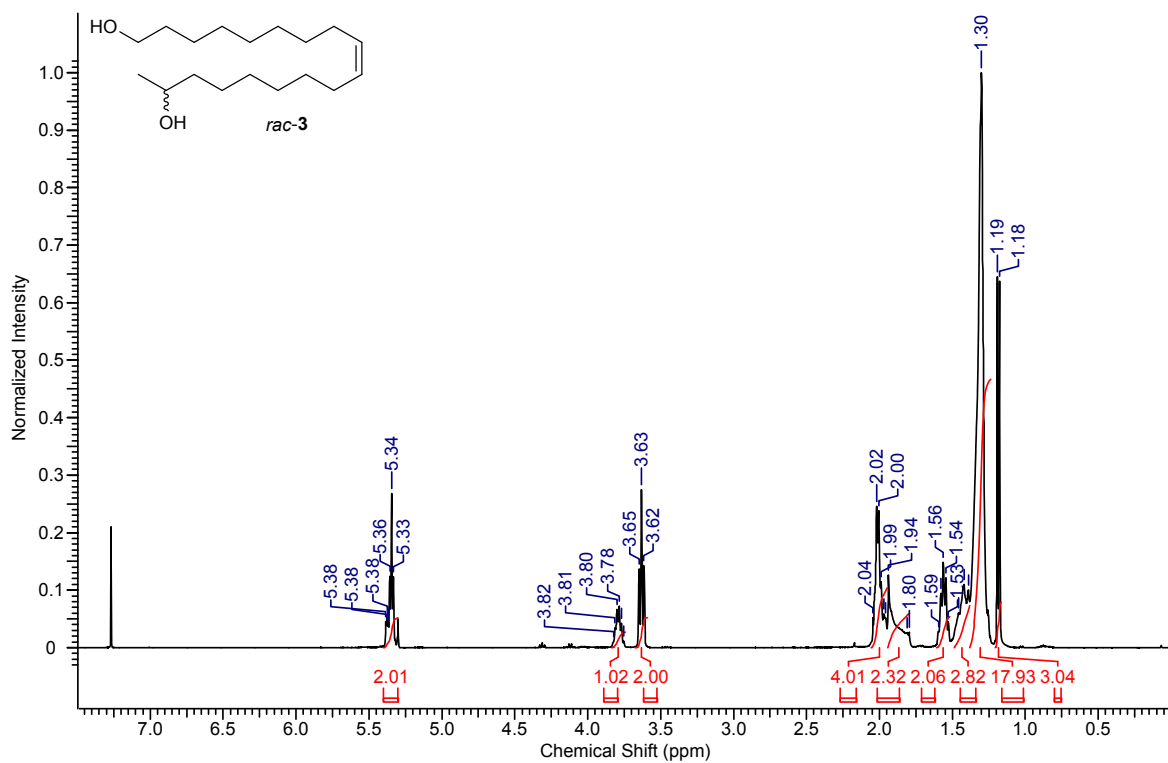
^{13}C NMR spectrum of compound *rac-6* in CDCl_3 (100 MHz)



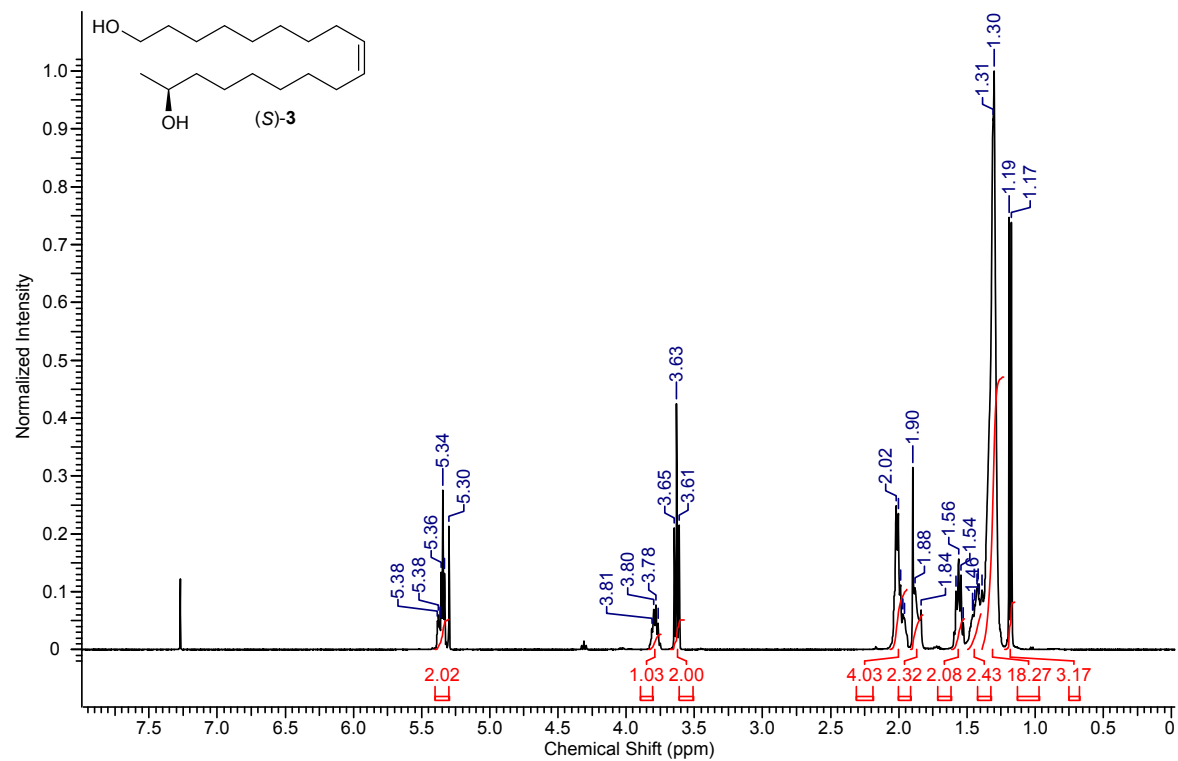
^1H NMR spectrum of compound (S)-6 in CDCl_3 (400 MHz)



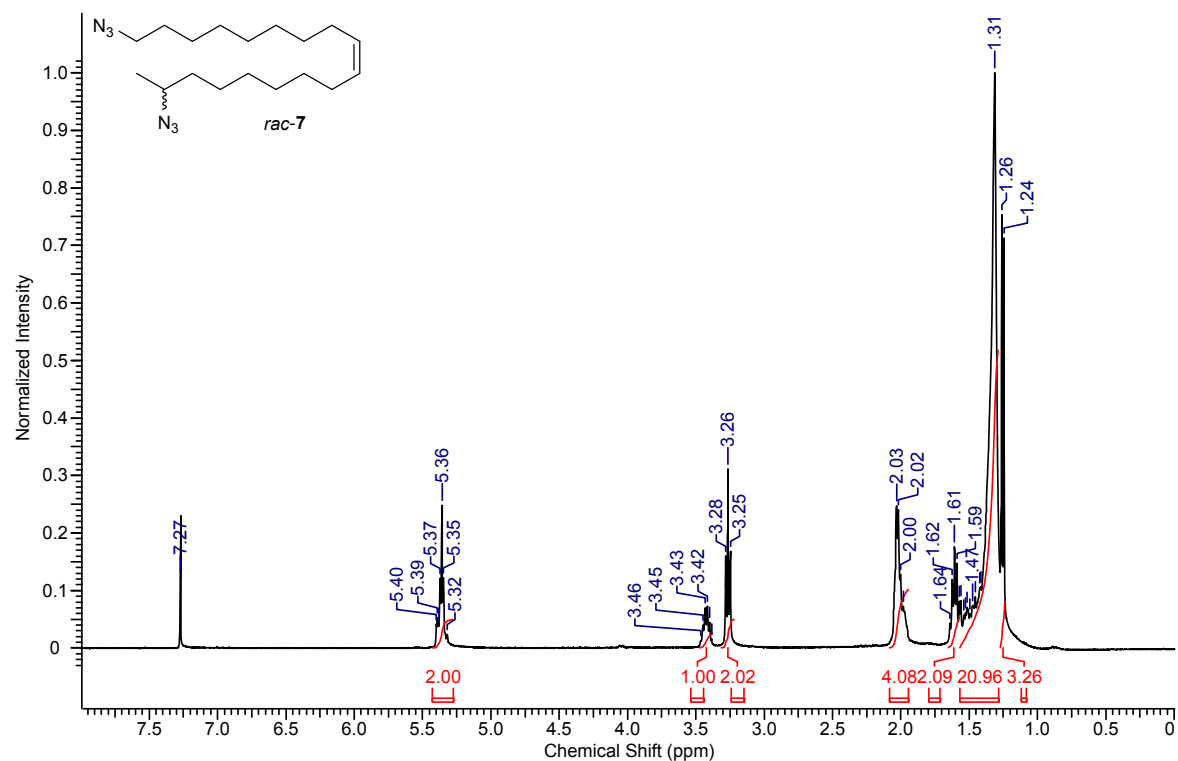
^1H NMR spectrum of compound *rac*-3 in CDCl_3 (400 MHz)



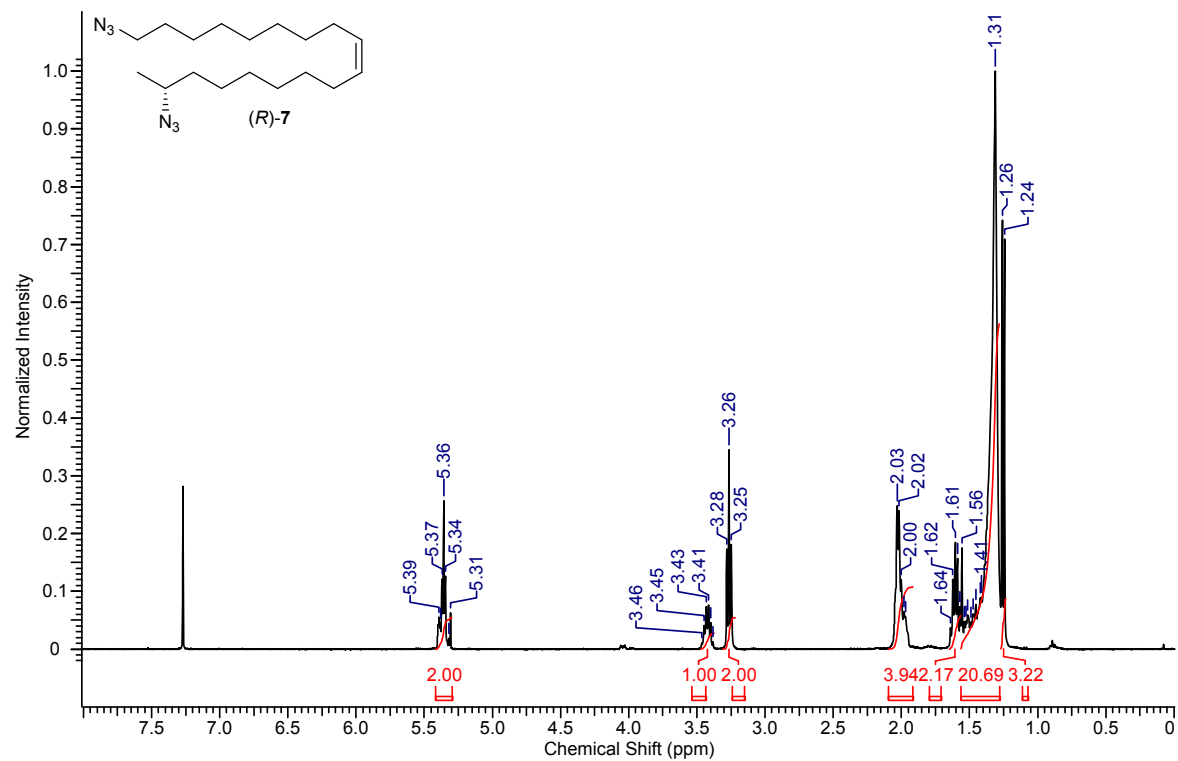
^1H NMR spectrum of compound (*S*)-**3** in CDCl_3 (400 MHz)



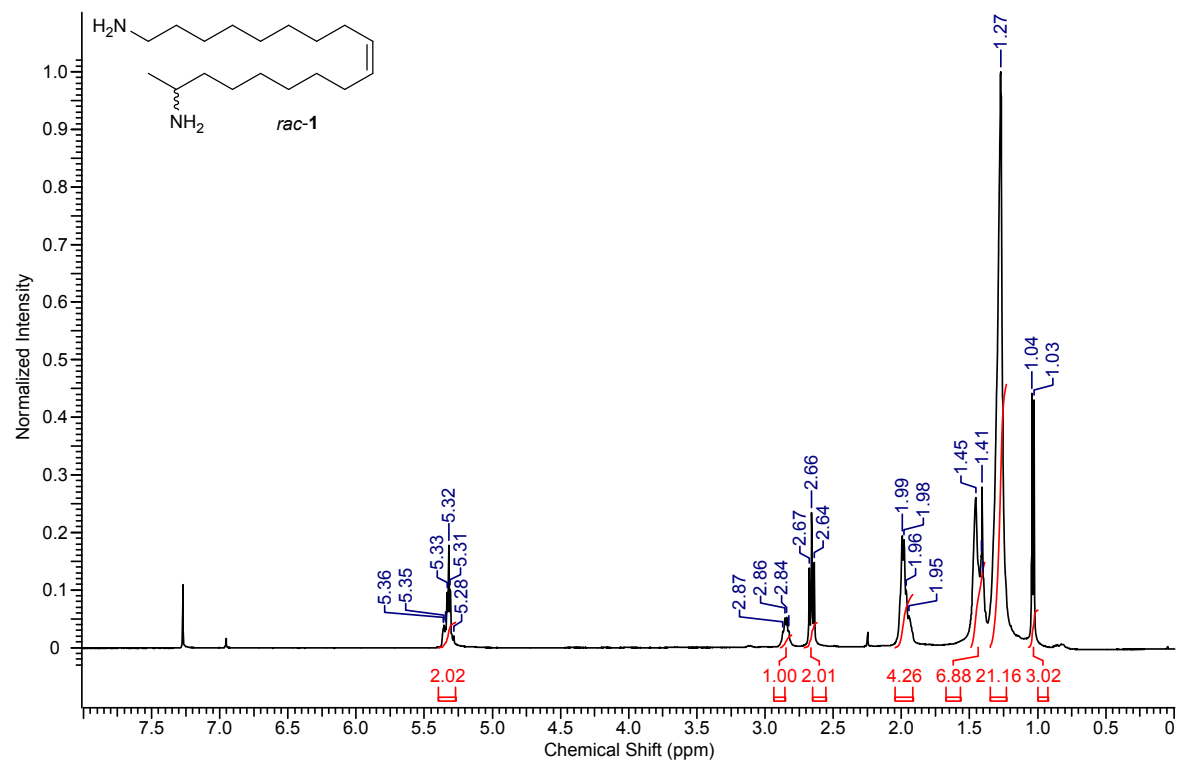
^1H NMR spectrum of compound *rac*-**7** in CDCl_3 (400 MHz)



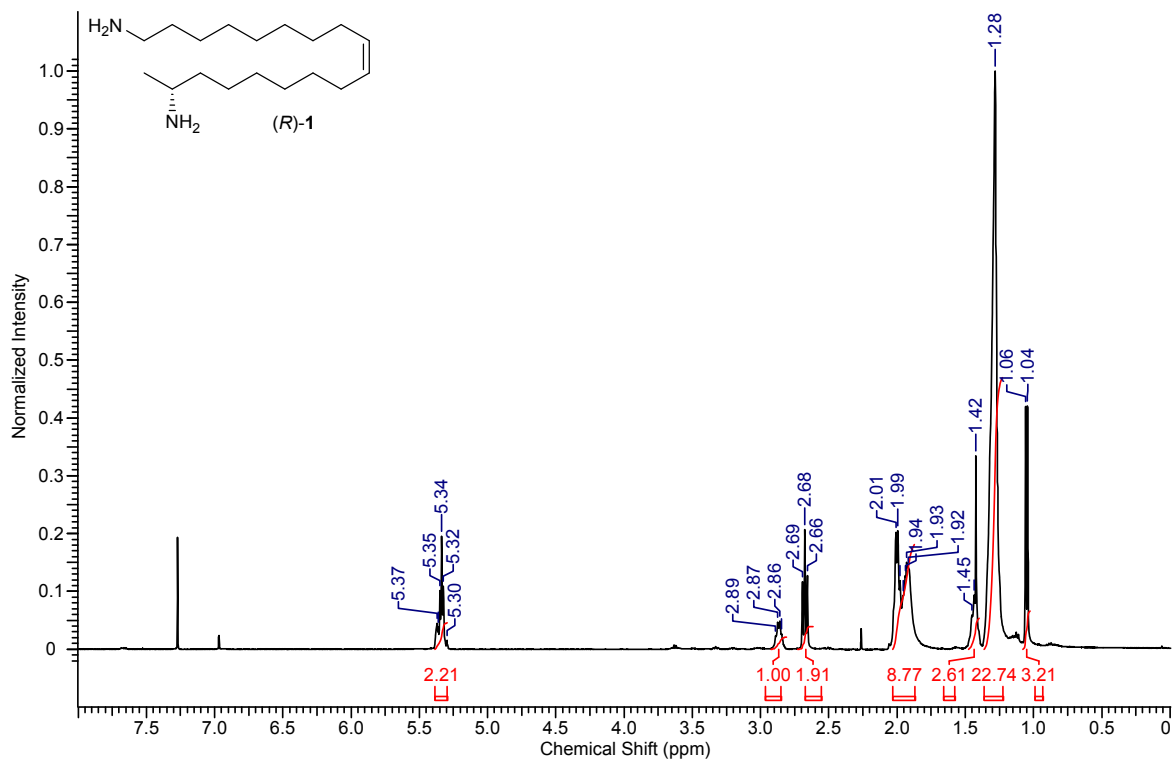
^1H NMR spectrum of compound (*R*)-7 in CDCl_3 (400 MHz)



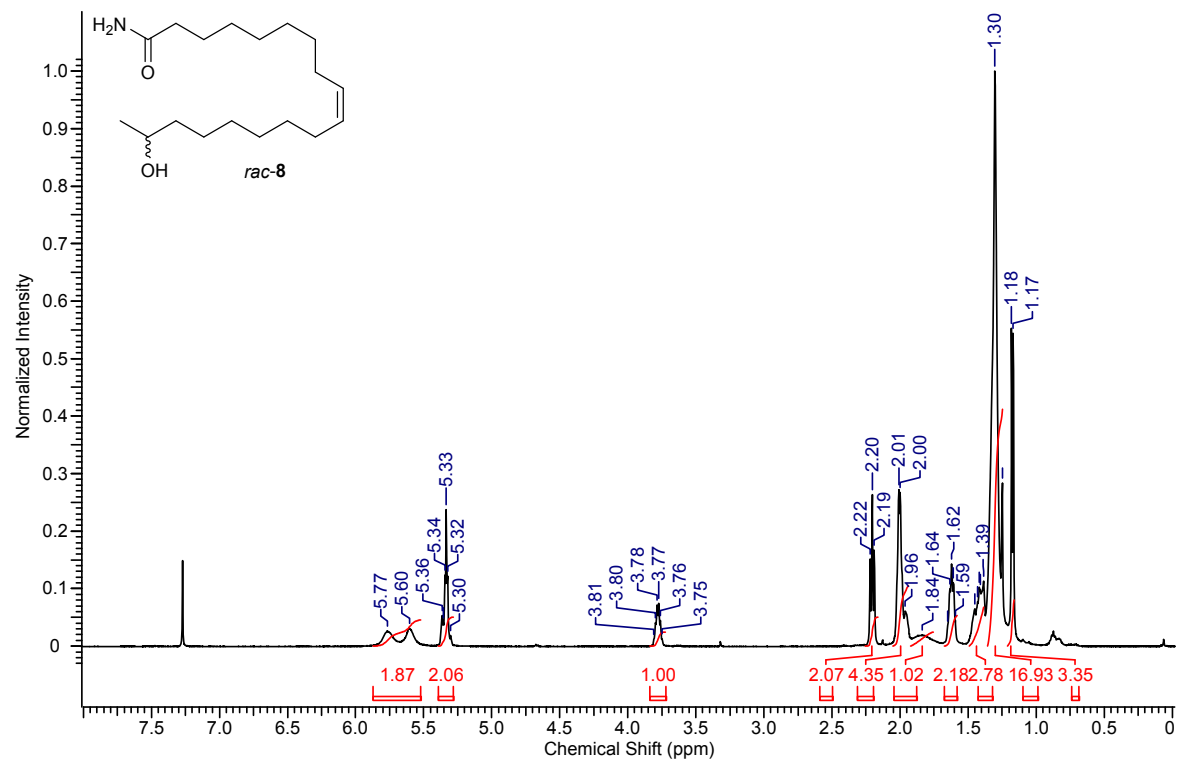
^1H NMR spectrum of compound *rac*-1 in CDCl_3 (400 MHz)



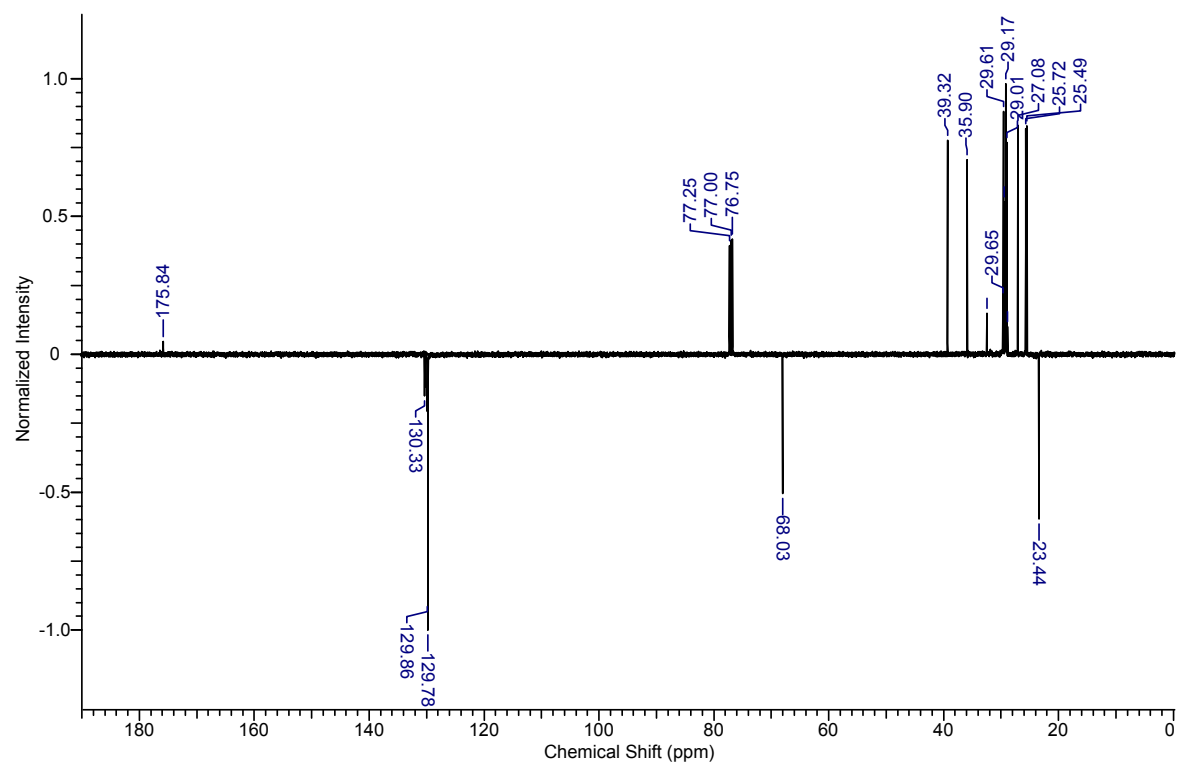
^1H NMR spectrum of compound (*R*)-**1** in CDCl_3 (400 MHz)



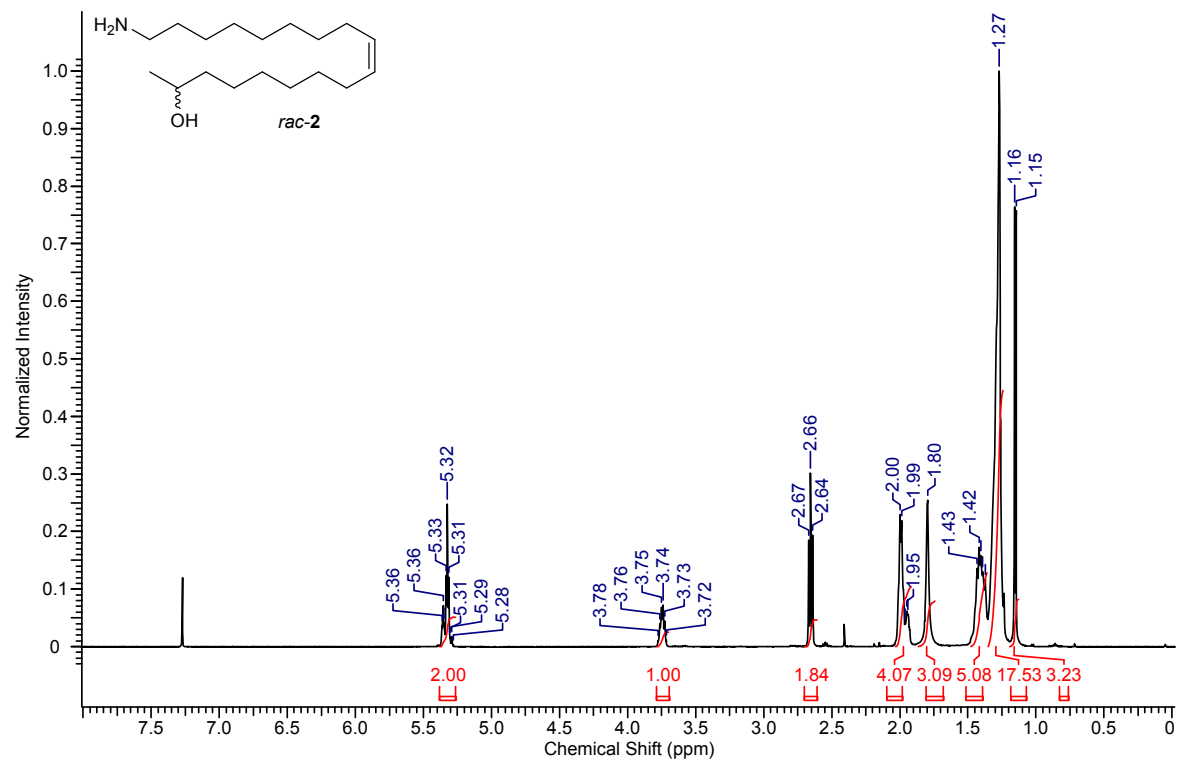
^1H NMR spectrum of compound *rac-8* in CDCl_3 (400 MHz)



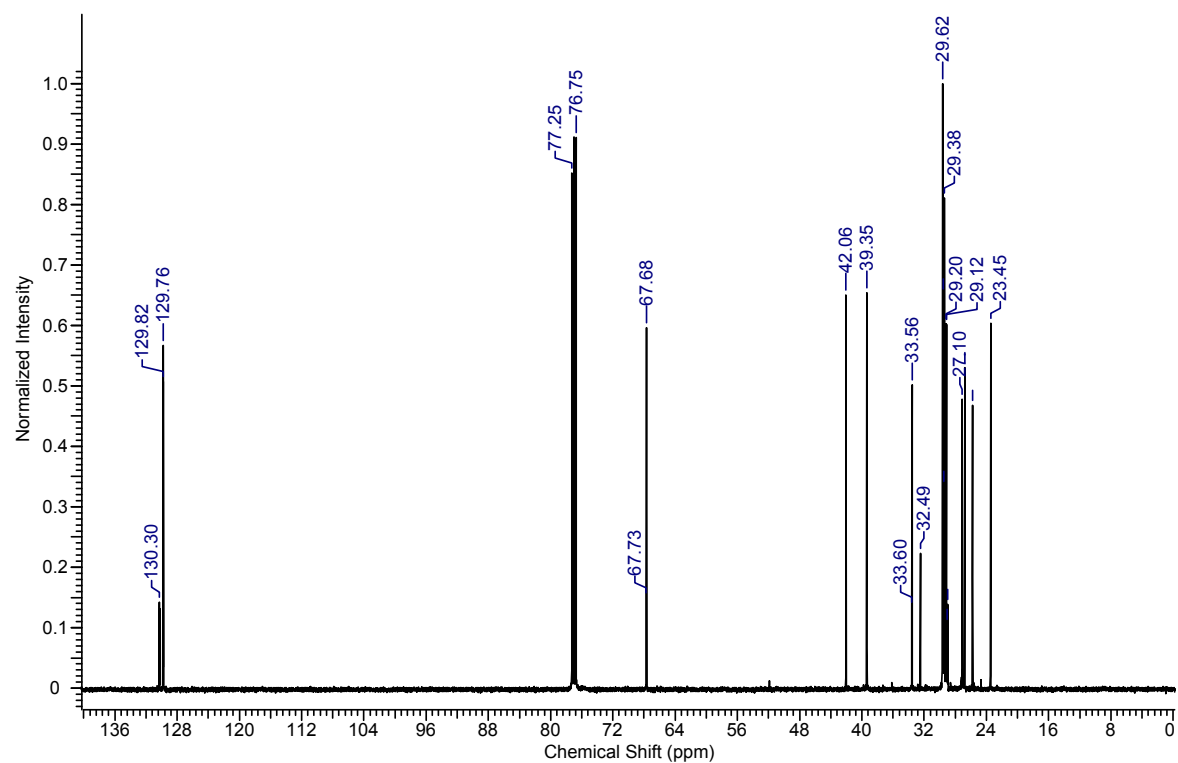
^{13}C NMR spectrum of compound *rac-8* in CDCl_3 (100 MHz) (Z/E 80/20)



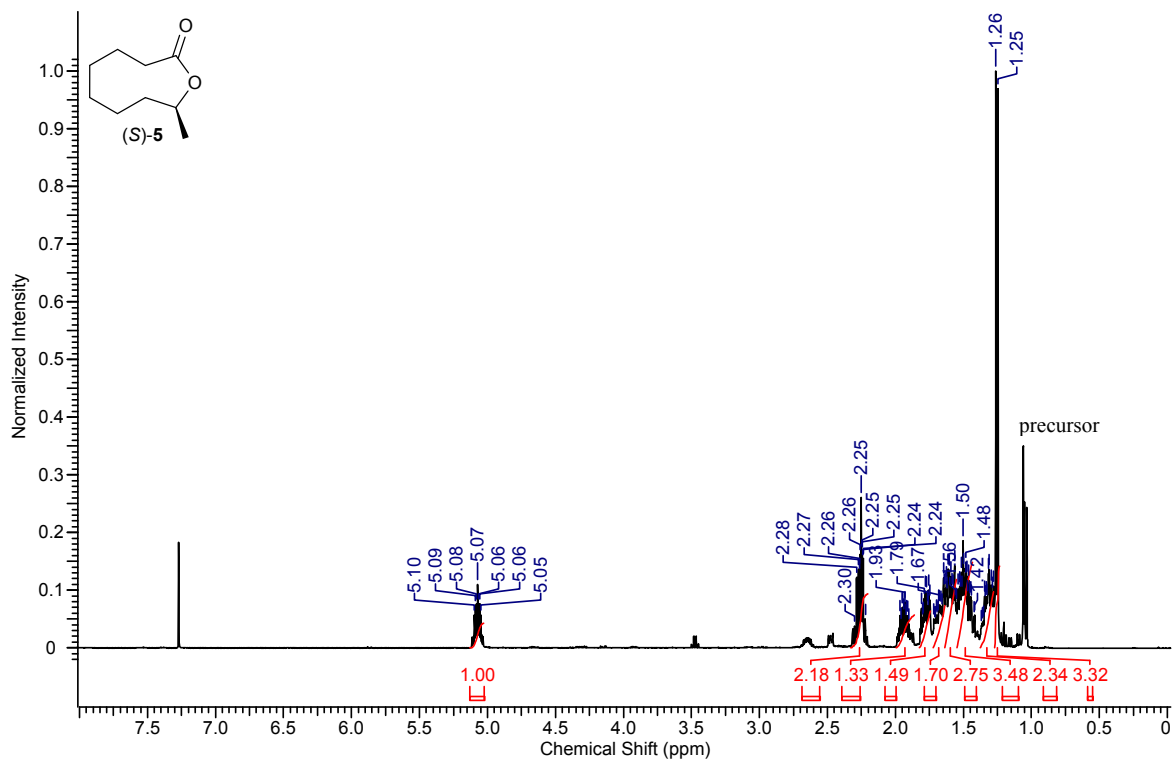
^1H NMR spectrum of compound *rac-2* in CDCl_3 (400 MHz)



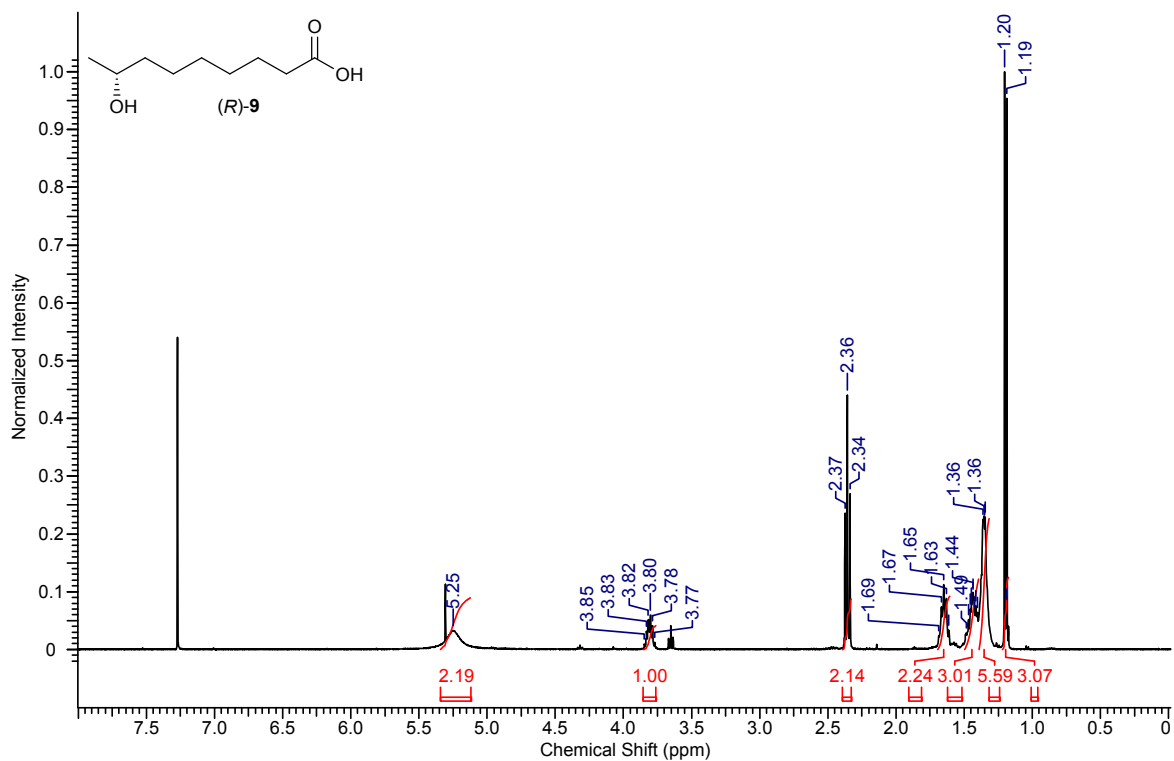
^{13}C NMR spectrum of compound *rac-2* in CDCl_3 (100 MHz) (Z/E 80/20)



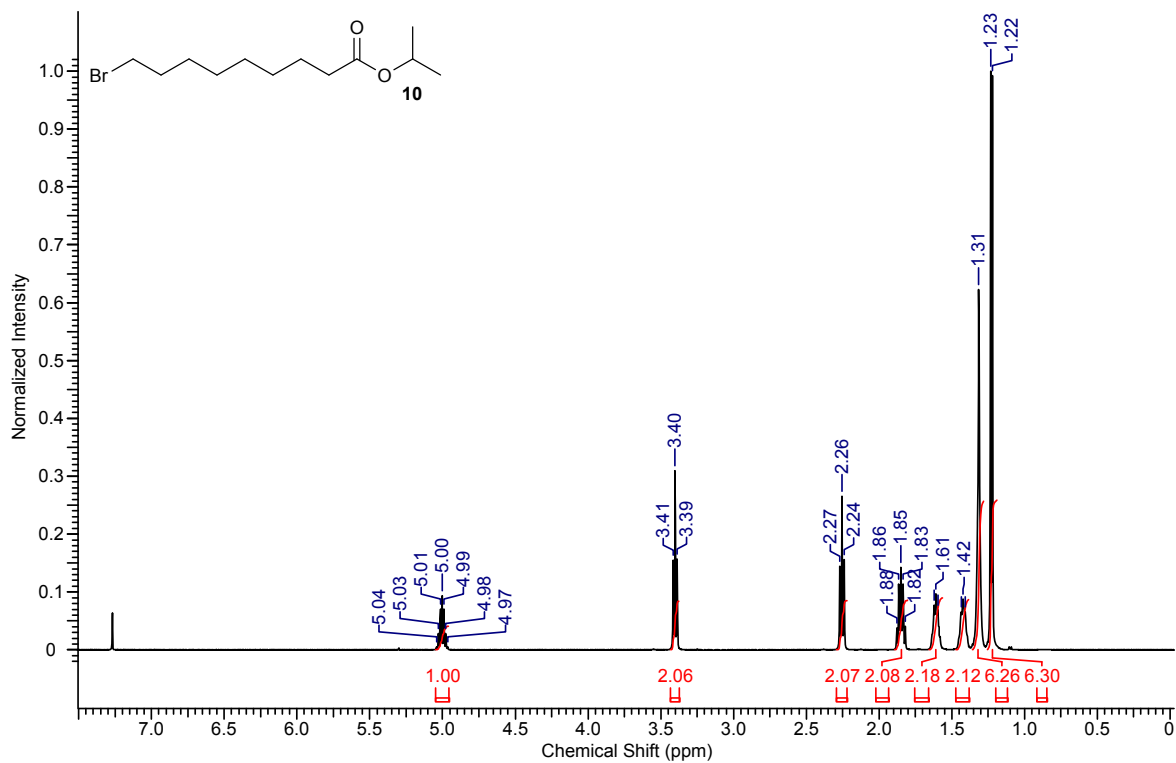
^1H NMR spectrum of compound (*S*)-**5** in CDCl_3 (400 MHz) (unpurified)



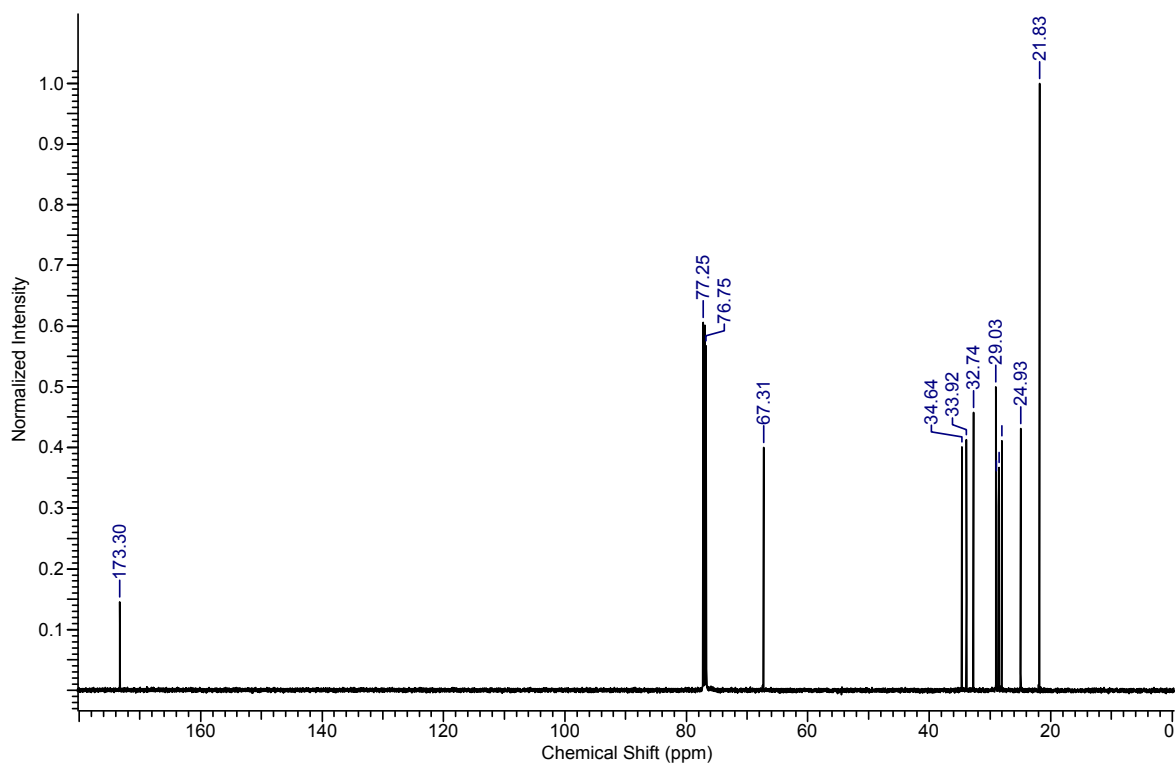
^1H NMR spectrum of compound (*R*)-**9** in CDCl_3 (400 MHz) (unpurified)



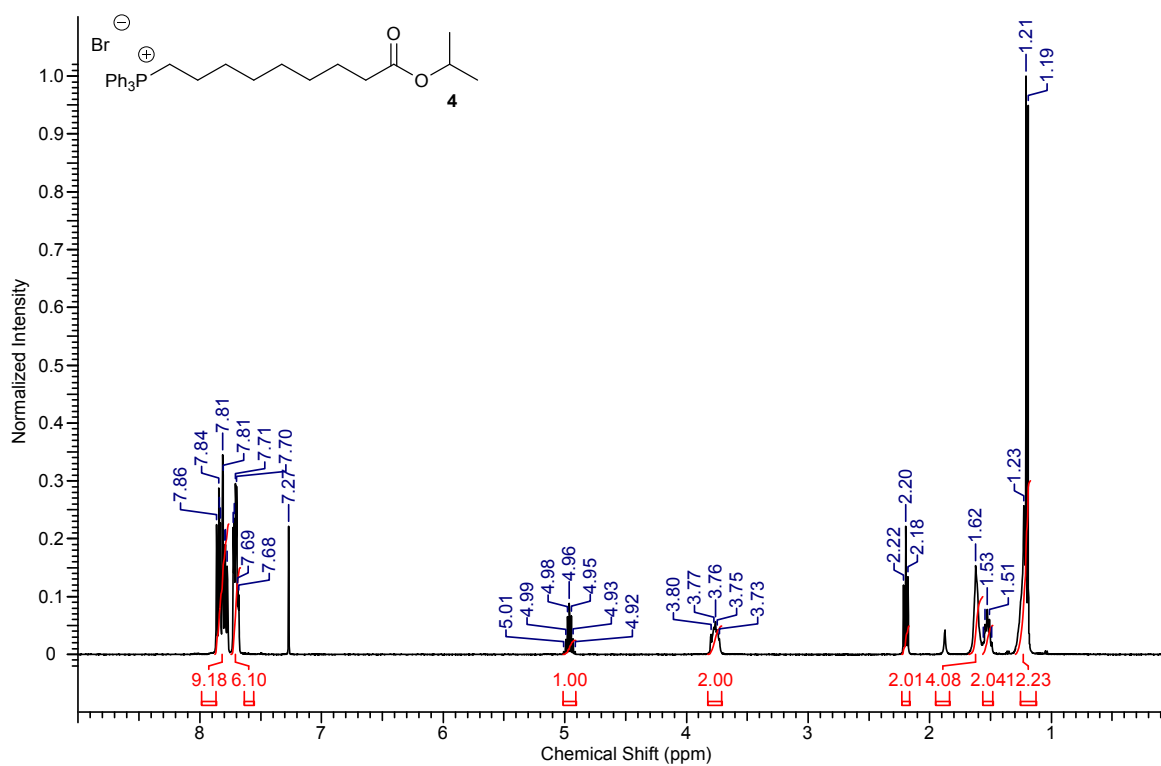
^1H NMR spectrum of compound **10** in CDCl_3 (400 MHz)



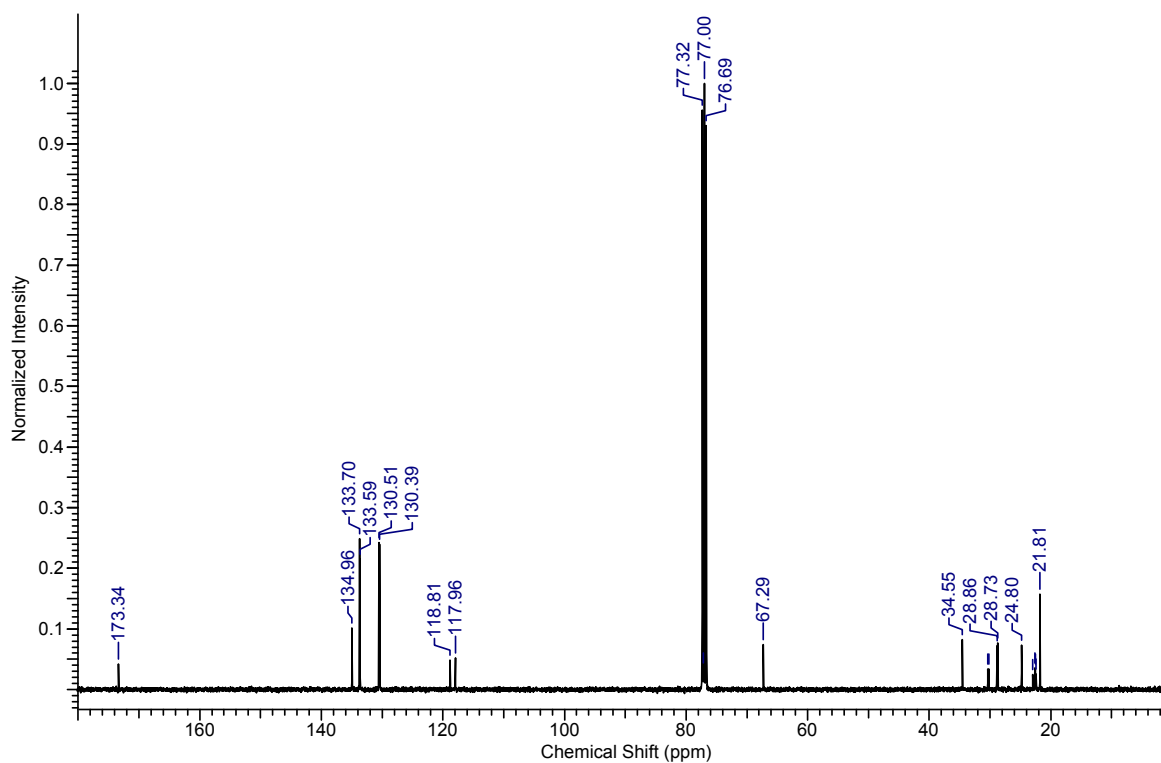
^{13}C NMR spectrum of compound **10** in CDCl_3 (100 MHz)



^1H NMR spectrum of compound **4** in CDCl_3 (400 MHz)



^{13}C NMR spectrum of compound **4** in CDCl_3 (100 MHz)



MS data

Isopropyl (9Z)-17-hydroxyoctadec-9-enoate (rac-6). MS (GC-MS, EI) *m/z* (%) 340 ([M]⁺, 0.3), 322 (1.5), 279 (22), 123 (28), 109 (56), 95 (82), 81 (92), 67 (83), 55 (100), 43 (74), 41 (71).

(9Z)-Octadec-9-ene-1,17-diol (rac-3). MS (GC-MS, EI) *m/z* (%) 284 ([M]⁺, 0.6), 266 (10), 149 (6), 135 (14), 124 (24), 110 (56), 96 (84), 95 (82), 82 (85), 81 (92), 67 (100), 55 (99).

(9Z)-Octadec-9-ene-1,17-diamine (rac-1). MS (HPLC, APCI) *m/z* (%) 283 ([M + H]⁺, 100), 264 (8).

(9Z)-17-Hydroxyoctadec-9-enamide (rac-8). MS (GC-MS, EI) *m/z* (%) 297 ([M]⁺, 1), 279 (2), 262 (5), 207 (11), 109 (28), 95 (53), 81 (63), 72 (64), 69 (39), 67 (60), 59 (94), 55 (100), 41 (72).

(9Z)-18-Aminooctadec-9-en-2-ol (rac-2). MS (GC-MS, EI) *m/z* (%) 283 ([M]⁺, 18), 268 (38), 250 (12), 238 (22), 222 (12), 210 (14), 196 (16), 182 (35), 168 (48), 154 (96), 140 (38), 123 (18), 109 (36), 95 (86), 81 (90), 79 (46), 67 (100), 55 (42);

(9S)- 9-Methyl-oxonan-2-one ((S)-5). MS (GC-MS, EI) *m/z* (%) 156 ([M]⁺, 0.6), 138 (11), 112 (59), 94 (32), 84 (81), 68 (100), 55 (94), 41 (60).

(8R)-4-Hydroxynonoic acid ((R)-9). MS (GC-MS, EI) *m/z* (%) 174 ([M]⁺, 0.1), 141 (16), 130 (28), 95 (26), 87 (56), 73 (100), 69 (20), 55 (32), 45 (71).

Isopropyl 9-Bromononanoate (10). MS (GC-MS, EI) *m/z* (%) 280, 278 ([M]⁺, 0.04), 265 (0.08), 263 (0.08), 239 (12), 237 (12), 221 (26), 219 (26), 157 (26), 139 (30), 102 (68), 97 (32), 73 (32), 69 (50), 60 (74), 55 (58), 43 (100), 41 (59).

Determination of the enantiomeric excess of (*R*)-**9**

Rac-**9** as well as enzymatically prepared (*R*)-**9** were derivatized with TMS-diazomethane and MSTFA. Separation was achieved on a β -6TBDM column (Figure 1).

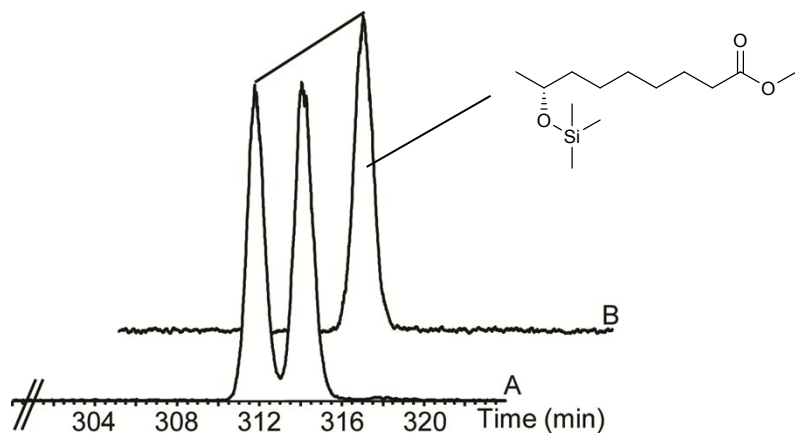
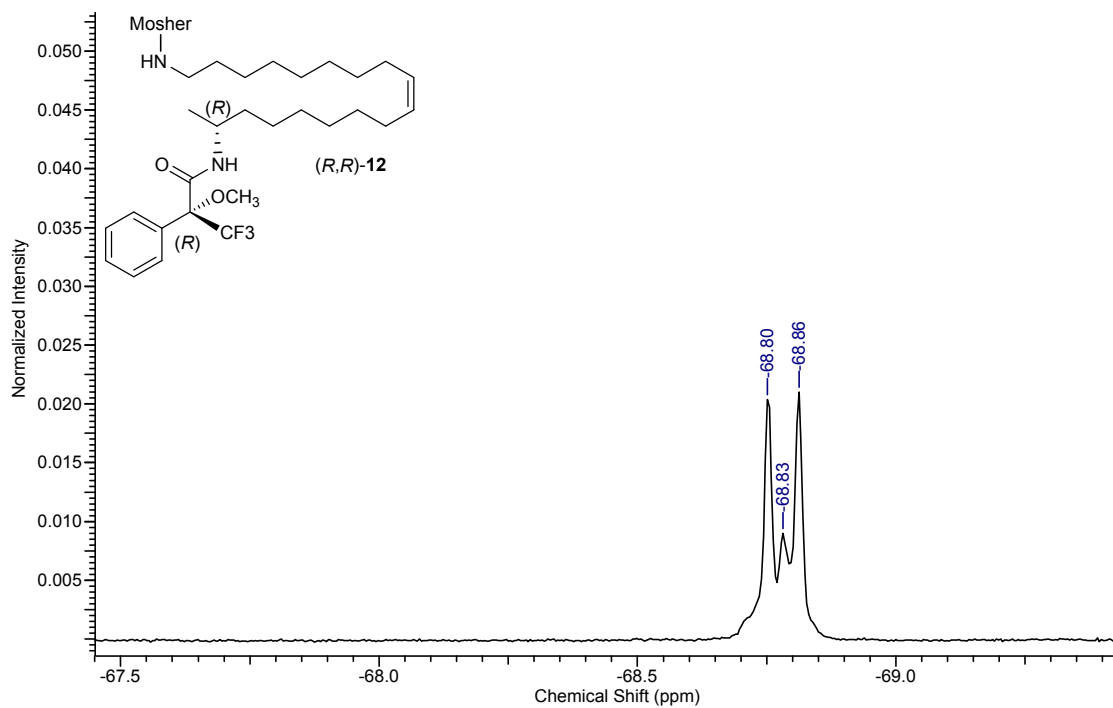


Figure 1. GC-MS spectra of A: derivatized racemic mixture *rac*-**9** and B: compound (*R*)-**9**; Determination of the ee of (*R*)-**9**: ee \geq 99 %. GC program: 60 °C (5 min), 0.1 °C/min \rightarrow 120 °C (5 min), 40 °C/min \rightarrow 200 °C (3 min).

^{19}F NMR spectrum of compound (*R,R*)-**12** in CDCl_3 (Z/E 80/20)



^{19}F NMR spectrum of compounds (*R,R*)-**12** and (*R,S*)-**12** in CDCl_3 (Z/E 80/20)

